

Thin Film Inorganic Electrochemical Systems
Final Technical Report
by

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Abstract: During the 21 month period of this contract we have studied components for an all inorganic thin film lithium ion cell. During this work we have determined that thin film cathodes of LiCoO_2 can be readily performed by either spray pyrolysis or spin coating. These cathodes are electrochemically active. We have also determined that thin film anodes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be prepared by spray pyrolysis or spin coating. These anodes are also electrochemically active (~1.6V versus lithium). The thermal processing of this anode is very critical if one wishes to avoid inert impurities (i.e., TiO_2 or Li_2TiO_3). Thin film electrolytes of $\text{Li}_{3.6}\text{Ge}_{.6}\text{V}_{.4}\text{O}_4$ have been prepared and tested in electrochemical cells with thin film cathodes of LiCoO_2 and thin film anodes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and been shown to function. This work has made substantial progress towards preparing an all inorganic lithium ion devise by simple chemical means.

Introduction: The goal of this work was to determine the feasibility of preparing all inorganic, thin film lithium ion cells by a simple chemical process (i.e., spray pyrolysis or spin coating). In the previous reports we have given details on the synthetic techniques used to prepare the various components (anodes, cathodes and electrolytes). In this final interim report we will discuss the electrochemical performance of the individual components prepared as well as total cells incorporating the three components.

Cathode Materials: Throughout this project we have prepared a variety of lithium cobalt dioxide thin films by spray pyrolysis or spin coating techniques. These electrodes have been easy to prepare and show activity in almost 100% of the samples examined (more than 30 thin film electrodes have been examined). We have noticed that the electrical conductivity of the material can obtain values as high as 0.2

Scm-1 if care is taken to prepare dense electrodes. We have also been able to prepare thicker electrodes much quicker than our standard spray process if we prepare a suspension by mixing fine LiCoO₂ powder with our standard sol. These electrodes also function electrochemically, although the kinetics of the electrode are somewhat slower (see figure 1 for a comparison of a standard sprayed electrode and a composite electrode prepared by this technique). We have also tried to prepare thin film cathodes of the spinel LiMn₂O₄ from techniques analogous to those used to prepare LiCoO₂. Although X-ray powder diffraction indicates that we have obtained single phase material with this structure, these electrodes are not reproducibly active. It is our feeling that the manganese system is far more complicated (easy substitution of lithium for manganese, formation of non active phases etc.) and reliable preparation of thin film manganese cathodes needs substantially more work.

The only somewhat troubling observation with our thin film LiCoO₂ cathodes is the continuous decrease in total reversible capacity with cycling. In our cycling tests all cells lost at least 50% capacity after 300 deep discharges. It is possible that this is due to electrolyte decomposition, since these cycling tests were done in contact with a liquid electrolyte (LiClO₄ in propylene carbonate). This loss in capacity with deep discharge must be studied in more detail, especially with the

elimination of the liquid electrolyte.

Anode systems ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiTi_2O_4 and Carbon): In previous reports we have described the spray pyrolysis and spin coating of thin films of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and LiTi_2O_4 . These films can be reproducibly prepared; however, they require a careful thermal treatment to avoid contamination with electrochemically inert phases (TiO_2 and Li_2TiO_3). In figure 2 is shown an X-ray powder diffractogram of a standard anode on Al foil using a particular thermal treatment that yielded excellent results. In figure 3 is shown a cyclic voltamogram of one of our standard anodes on Al foil. As with the LiCoO_2 cathodes the sprayed or spun electrodes are almost always electrochemically active showing performance similar to that shown in figure 3. We feel that this material is a promising anode material that should be compared in detail with carbon for lithium ion cells. Although the voltage is slightly higher versus lithium, there is no irreversible lithium uptake that will cause capacity loss. We have prepared thin films of amorphous carbon electrodes by gas phase pyrolysis (or CVD) using toluene as a precursor at 900°C . These films are also electrochemically active; however, the high preparation temperature required the use of nickel foil as the substrate. Additional work should be performed to compare these two systems as thin film anodes in solid state cells.

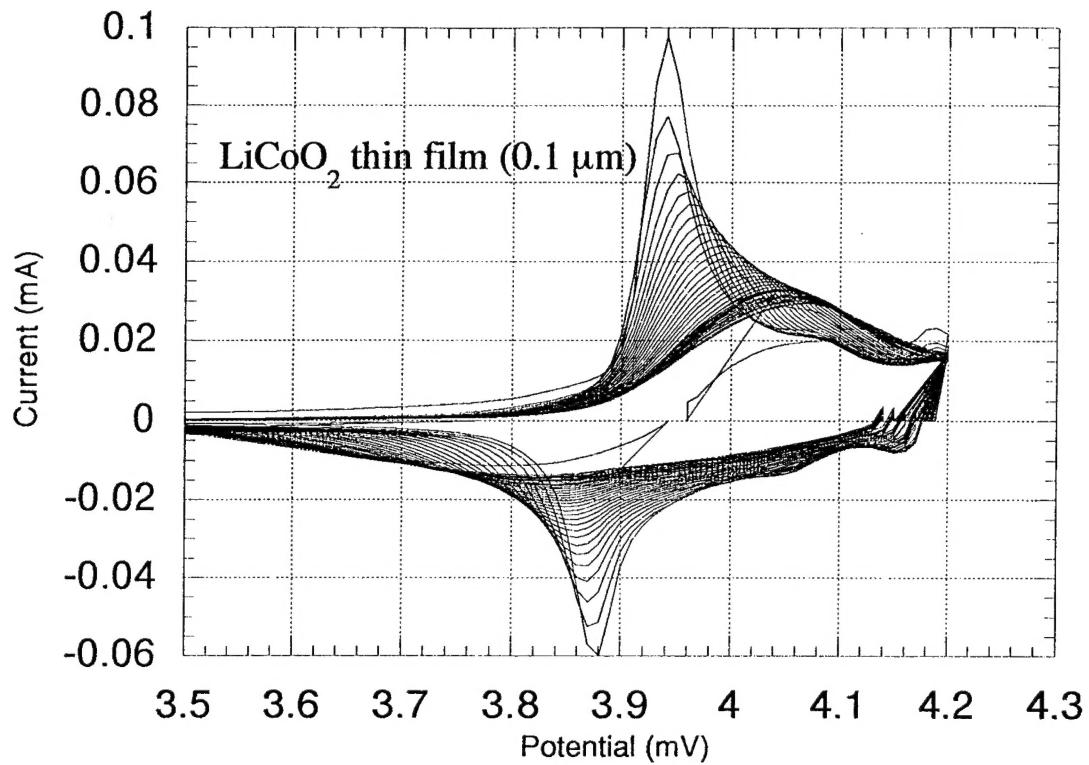
Electrolytes ($\text{Li}_{3.6}\text{Ge}_{.6}\text{V}_{.4}\text{O}_4$): Although we have prepared a variety of thin film electrolytes by spray pyrolysis and spin coating ($\text{Li}_{3.6}\text{Ge}_{.6}\text{V}_{.4}\text{O}_4$, $\text{Li}_3\text{Zn}_{.5}\text{GeO}_4$ and $\text{La}_{.67-x}\text{Li}_{3x}\text{TiO}_3$), due to limitations in time we felt that electrochemical cells could only be prepared from one of the compounds, and we selected $\text{Li}_{3.6}\text{Ge}_{.6}\text{V}_{.4}\text{O}_4$. Since the detailed use of this solid electrolyte in a thin film system would require substantial work, we opted to quickly study the possible functioning of this electrolyte by preparing cells with this compound deposited onto LiCoO_2 . The electrochemical contact to the anode was performed by using either a filter paper exposed to one drop of our standard liquid electrolyte or polyethylene oxide containing LiClO_4 . In figure 4 is shown a cyclic voltamogram of a total cell composed of a LiCoO_2 cathode, a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode and a dual electrolyte $\text{Li}_{3.6}\text{Ge}_{.6}\text{V}_{.4}\text{O}_4/\text{LiClO}_4$ + propylene carbonate. This cell as well as two other cells prepared using polyethylene oxide in place of the propylene carbonate have reversibly cycled at the potentials expected. No other peaks indicative of electrolyte decomposition were observed.

These initial results on the cathode/electrolyte interface indicate that this particular solid state electrolyte shows promise for the inorganic thin film cell. Additional work needs to be done to examine the anode/electrolyte interface and finally the total inorganic cell must be prepared prior to determining that this electrolyte is a

good candidate. In addition further studies should compare the performance of $\text{Li}_{3.6}\text{Ge}_{1.6}\text{V}_{4.4}\text{O}_4$ with $\text{Li}_3\text{Zn}_{1.5}\text{GeO}_4$ and $\text{La}_{1.67-x}\text{Li}_{3x}\text{TiO}_3$.

Conclusions: During the limited time of this project we feel that substantial progress has been made in the development of an all inorganic, thin film cell prepared by simple chemical techniques. Thin film anodes and cathodes can be reliably prepared. We have also shown that a cathode/solid state electrolyte interface seems to be stable and capable of functioning electrochemically. Additional work needs to verify that the electrolyte/anode interface is also electrochemically active prior to preparing total cells. In addition, studies should be performed on the other two electrolyte systems we developed for this program (i.e., $\text{Li}_3\text{Zn}_{1.5}\text{GeO}_4$ and $\text{La}_{1.67-x}\text{Li}_{3x}\text{TiO}_3$) to determine the optimum system.

Slow scan cyclic voltamogram (10 mV/10 sec) thin film LiCoO_2
versus a lithium reference electrode



Slow scan cyclic voltamogram (10 mV/10 sec) of a composite
thin film LiCoO_2 (the LiCoO_2 solution sprayed contain
 LiCoO_2 powder) versus a lithium reference electrode

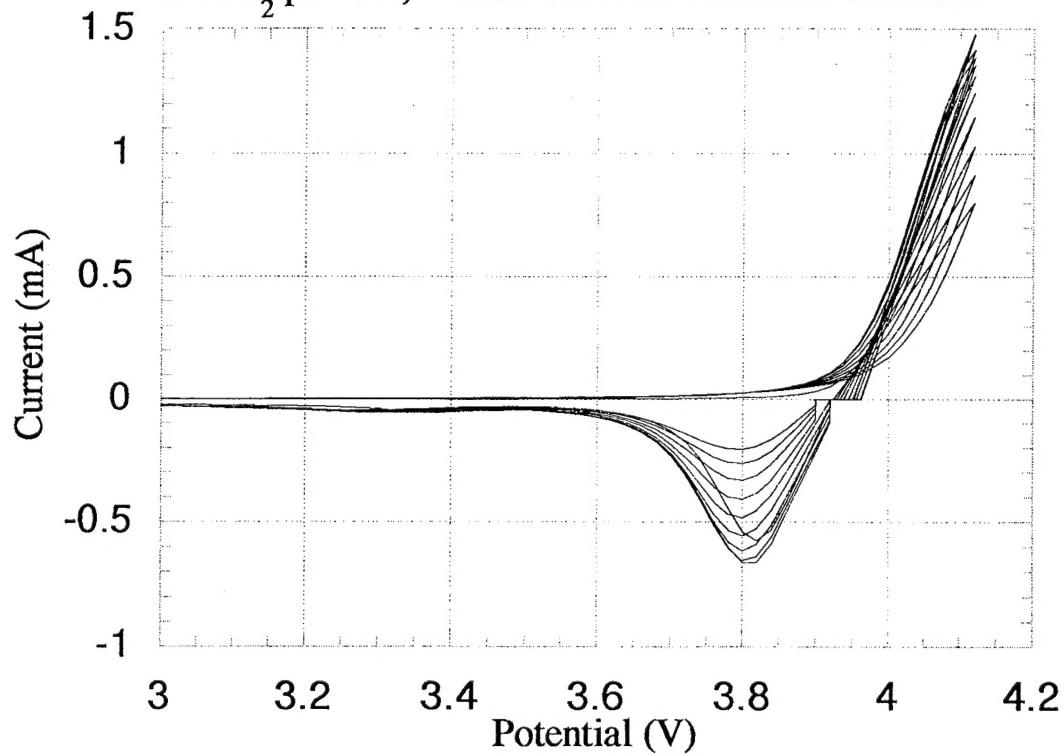


Figure 1

Li₄Ti₅O₁₂ powder from a spray on Al foil

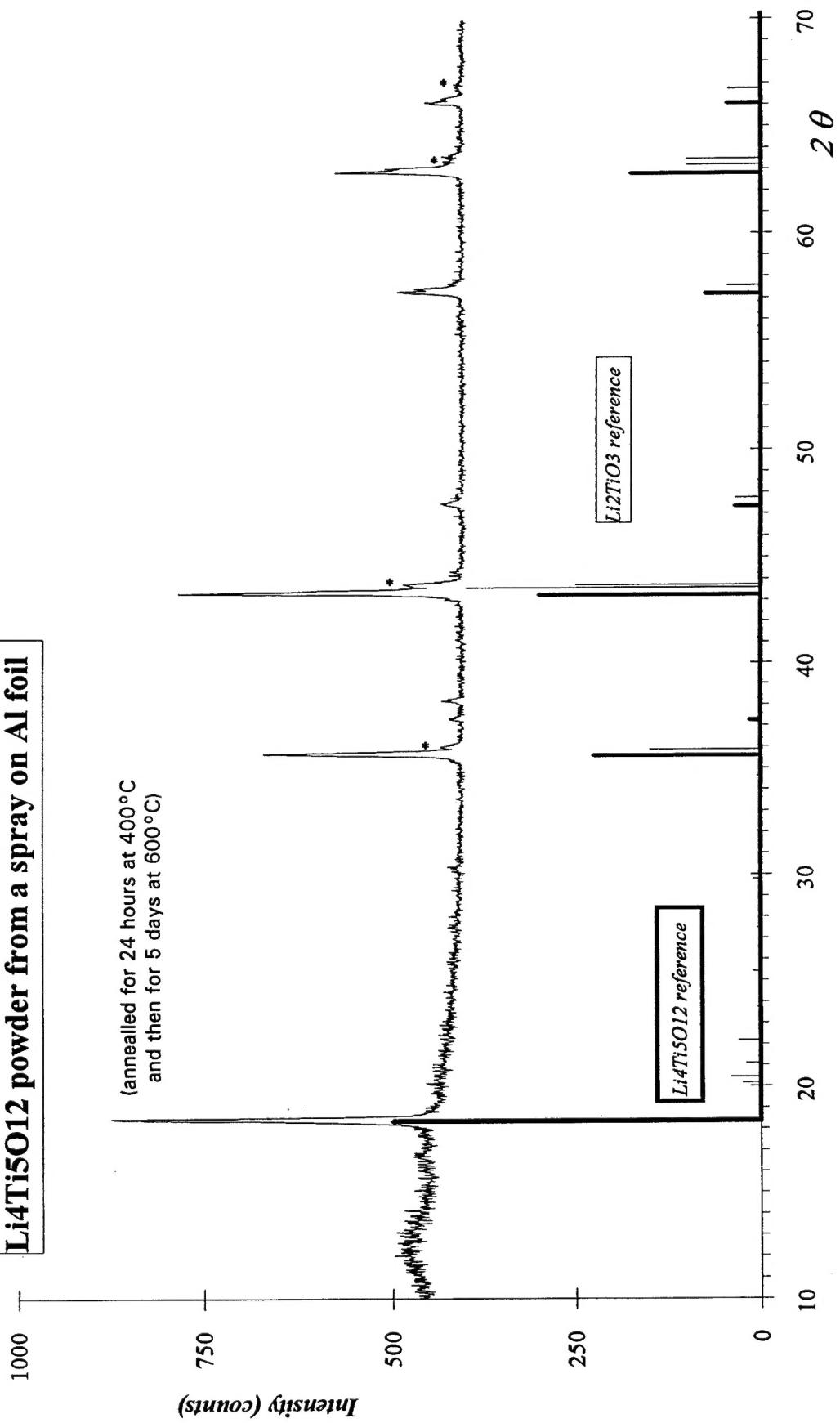


Figure 2

Slow scan cyclic voltamogram (10 mV/10 sec)
of thin film $\text{Li}_4\text{Ti}_5\text{O}_{12}$ versus a lithium reference electrode

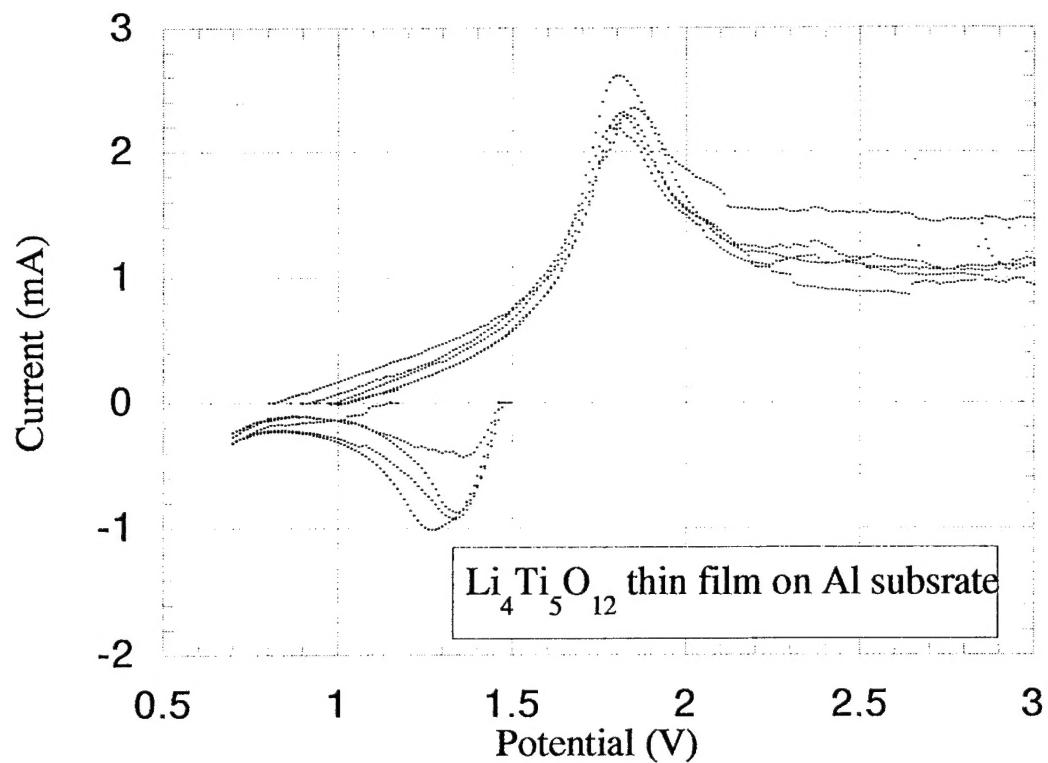


Figure 3

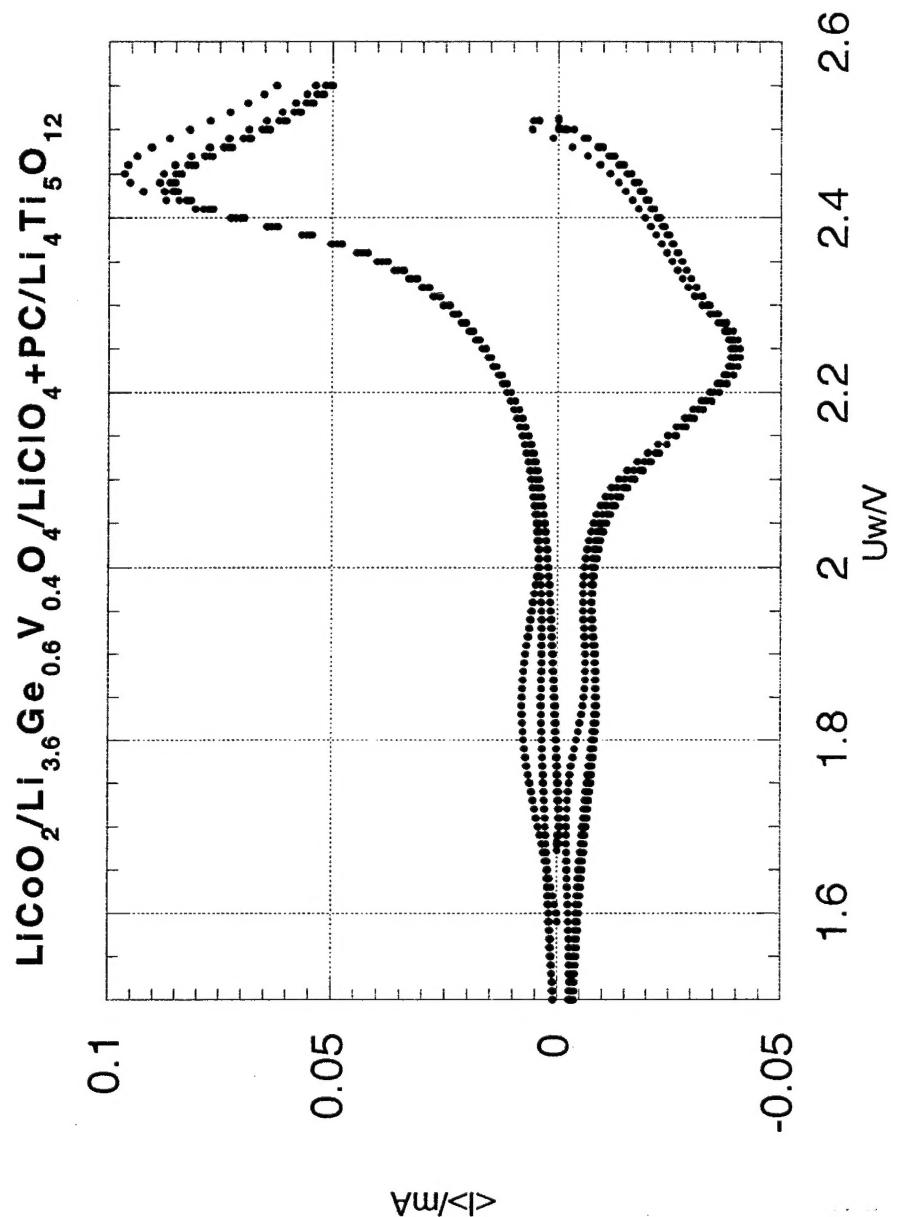


Figure 4